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# The Evolution of Ultrahigh Carbon Steels — From the Great Pyramids, to Alexander the Great, to Y2K

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# THE EVOLUTION OF ULTRAHIGH CARBON STEELS — FROM THE GREAT PYRAMIDS, TO ALEXANDER THE GREAT, TO Y2K

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**Abstract**

Hypereutectoid steels containing between about 1 and 2.1 wt%C, and now known as ultrahigh carbon steels (UHCS), have both a rich history (dating back to the time of Alexander the Great, i.e. ~300 BC) and an interesting, recent, technological period of development (from 1975 to the present). The connections between the modern UHCS and their ancient counterparts, and in particular Damascus steels, have received considerable attention. In addition to monolithic products, UHCS have also been used in both ancient and modern times in laminated composites. In the present paper, a summary of the modern development of UHCS and UHCS-containing laminates is given, and parallels are drawn with ancient materials. Also, ancient laminated composites containing other steels are described; controversial issues and a possible solution related to the age of such a laminate found in the Great Pyramid of Gizeh are discussed.

## Introduction

The present paper has its origins in the development of a modern family of steels — the ultrahigh carbon steels (UHCS) — this family has direct similarities in composition to certain ancient steels. The UHCS, which contain relatively large amounts of carbon (between 1 and 2 wt%), were developed at Stanford University from about 1975 to the present time. Their high carbon content was subsequently recognized to be similar to that found in Damascus steels and, upon further studies, to other ancient steels, including the Japanese *tama-hagane* (a material of 1.6%C that is reduced to 0.6 to 1.0%C by folding) and English crucible steel (1.0%C). Also, as laminated composites were developed that contained UHCS, parallels were drawn with ancient composites that in some cases also contained high carbon steels. The various facets of the UHCS invention, development, and links to the past are described in 112 papers (including six patents). A recent review summarizes this material.(1)

The modern UHCS were initially developed for the property of superplasticity, i.e., the ability to undergo large plastic tensile strains (over several hundreds to thousands of percent). In seeking to meet the microstructural requirements for superplasticity, Oleg D. Sherby and his colleagues recognized the necessity to increase the carbon content from the range utilized in traditional, contemporary steels (which reaches a maximum at about 1%C for bearing and tool steels). In doing so, they ventured into the relatively unexplored region of the iron carbon diagram between conventional plain carbon steels (0.1 to 1%C) and cast irons (over 2%C). Steels in this intermediate region had, from the end of the last century, been regarded in the literature as brittle and unworkable, and yet without the redeeming qualities (e.g. low melting point and castability) of the cast irons. It was a surprise then, that the UHCS developed in the late 1970s not only exhibited the excellent superplasticity for which they were designed, but they also had excellent room temperature ductility. Subsequently, alloys of UHCS were developed; the purposes of the alloying additions have been recently reviewed.(1) Although the tensile ductility of all the UHCS were excellent, the impact toughness of UHCS was less impressive; and so a program was undertaken whereby they were laminated to other, more tough, materials. This approach lead to surprising improvements in toughness in the laminated composites.

In the present paper, some highlights are given on modern UHCS, ancient UHCS, modern laminated composites containing UHCS, and ancient laminated composites. Also, a brief description is given of a steel plate found in the ancient Pyramid at Gizeh. The controversial implications of the steel plate being contemporaneous with the building of the Pyramid are discussed and a possible resolution of the issue is proposed.

## Ultrahigh Carbon Steels (UHCS)

Ultrahigh carbon steels (1.0 to 2.1%C), now designated as UHCS, have been viewed for most of this century as belonging in the “no man's land of carbon steels” being sandwiched between the extensively-utilized high carbon steels (0.6 to 1.0%C) and the mass-produced cast irons (2.1 to 4.3%C). This is depicted in Fig. 1 which illustrates a historical version of the most famous phase diagram, the binary Fe-C system. It took many years to complete this diagram beginning with the work of Tchernoff of Russia (1868), followed by Sauveur of the United States (1896), by Roberts-Austen of England (1897), by Roozeboom of Holland (1900); the diagram was completed by Honda of Japan (1920). Even then, the E point (the maximum solubility of carbon in austenite) was erroneously labeled at 1.7%C and not rectified until 1948 to its correct position at 2.1%C. Beyond 4.3%C (in the diagram of Fig. 1), is the iron carbide region since the majority of the structure consists of iron carbide (65 to 100% from 4.3 to 6.67%C).

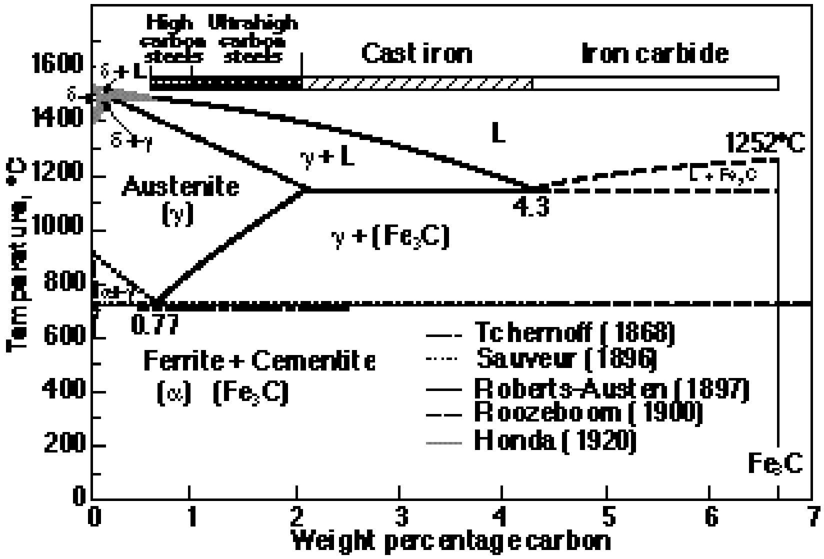


Figure 1. Historical description of the Fe-C phase diagram.

The origin of the belief that steels containing over 1%C were brittle can be traced to the classic work of Howe, published in 1891, in which the tensile ductility of steel was studied as a function of carbon content. The tensile ductility was shown to decrease dramatically with increasing carbon content and to become roughly constant, at a low value of 2 to 3%, in the region of UHCS. The primary reason for the low ductility in these UHCS is the result of the formation of a continuous, thick network of brittle iron carbide that forms in high carbon steels upon cooling from high temperature to intermediate temperature (for example, from 1000°C to 723°C for an Fe-1.6%C alloy). An example is shown in Fig. 2 of such an iron carbide network for a 1.6%C steel. These thick, continuous networks are locations at which cracks can initiate because iron carbide is brittle at room temperature and cracks within it will readily propagate under stress causing premature failure in the steel.

Over the last twenty years or so, initially at Stanford University and then at the Lawrence Livermore National Laboratory, procedures have been developed to eliminate the continuous carbide network in UHCS. The result is that relatively-homogeneous structures containing fine, equiaxed ferrite grains and fine, uniformly-distributed, spheroidized carbides are readily achieved. The range in tensile ductilities for UHCS containing 1.8%C can extend from 2 to 25% reflecting different morphologies and strengths produced by various processing routes.(2)

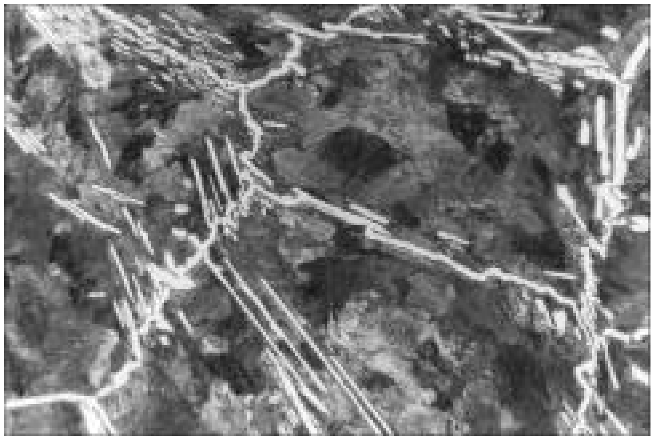

Figure 2. Modern UHCS showing a cementite network. The background structure is pearlite. (Magnification about 200 diameters.)

Superplasticity in UHCS

Superplasticity is the ability of certain crystalline materials to undergo very large tensile strains of up to 1000% and more. Superplasticity occurs at high temperatures and can revolutionize the manufacturing industry because superplastic materials can be formed into complex shapes. Superplastic forming can reduce or eliminate many of the welding, cutting, machining, and grinding steps that account for over a third of the cost of making most structural steel components. The main attribute required to make a metallic material superplastic is that it has to be fine-grained. In order to keep the grains fine at high temperature, it is usually necessary to have a second phase. Other conditions also are required, but the above two characteristics are the most well known. The existence of fine grains permits deformation by a grain boundary sliding process which gives the material a viscous-like property (the strain-rate sensitivity is high) and superplastic characteristics are achieved.

In 1973, it was predicted that it was possible to achieve this condition in plain carbon steels, but that they would have to contain a very high carbon content. Contrary to popular belief, iron carbide is not brittle at intermediate and high temperatures, and a network-free material was developed by continuously mechanically working the UHCS (1.3%, 1.6% and 1.9%C) as they were cooled from a white hot temperature (1200°C). This mechanical working (by either rolling or forging) broke up the iron carbide networks as they were first forming during cooling, i.e. at a point at which they were still thin and not fully continuous. Examples of the fine microstructures developed in a 1.5%C steel are shown in Fig. 3. This material is superplastic at high temperature and, of equal importance, is strong and ductile at room temperature. An example of a superplastically stretched UHCS sample is shown in Fig. 4, in which an elongation of over 1000% was achieved at 750°C with no evidence of imminent failure. The strain rate was 200% per minute.

The initial studies on superplasticity were essentially on unalloyed UHCS. Various thermomechanical processes were used including hot and warm working (HWW), isothermal warm working (IWW), divorced eutectoid transformation (DET), and divorced eutectoid transformation with associated deformation (DETWAD).(3, 4) It was also shown (5) that thermal cycling heat treatment of cast UHCS could lead to a fine structure and superplasticity.

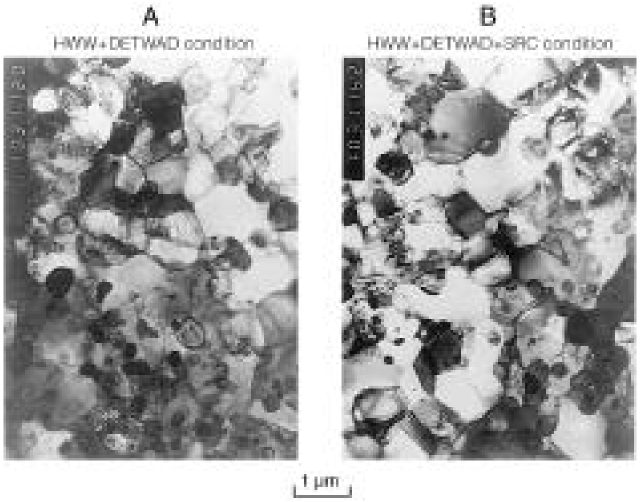


Figure 3. A 1.5%C UHCS material processed to obtain an ultrafine grain size. Left: as-processed condition. Right: deformation at 700°C. The light-colored grains are iron; the dark particles are iron carbide.

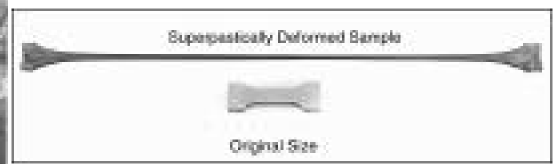


Figure 4. Superplastic behavior in a UHCS containing about 1.8%C.

Composition changes to enhance superplastic behavior of UHCS were carried out including small additions of chromium, vanadium, molybdenum, tungsten, and nickel.(6-9) It is worth noting that, in an attempt to study the superplastic behavior of plain carbon UHCS in a more scientific and fundamental manner, an attempt was made to study high purity Fe-C alloys. Walser, Kayali, and Sherby (10, 11) made the unexpected discovery that the high purity Fe-C alloys (1.6% and 1.9%C) could not be made superplastic indicating the importance of the normal additives in steel (such as Mn and Si) in retarding and controlling the growth of grains and cementite particles.

Extensive research was performed on the influence of silicon and aluminum in enhancing the superplastic behavior of UHCS. Alloying elements such as aluminum and silicon stabilize the ferrite phase, thus increasing the transformation temperature and the range of superplastic behavior. The strain-rate sensitivity exponent can also approach unity ($m = 1$) at high temperatures and low strain rates in a 10Al-1.2C UHCS material.(12)

It was also predicted that a strain rate sensitivity exponent equal to $m = 0.33$ would be observed at high strain rates. Such a respectably high strain rate sensitivity leads to quite high elongations of 200 to 300%.(13) This behavior is shown in Fig. 5 in which the flow stress is plotted as a function of the strain rate for three UHCS containing 7 to 10% aluminum. Superplastically formed parts were made from a UHCS-high Al material and commercialization of large ring components was intended by Sulzer Brothers of Winterthur, Switzerland, but the project was abandoned because no steel producer was prepared to make the fine-grained UHCS-high Al alloy.

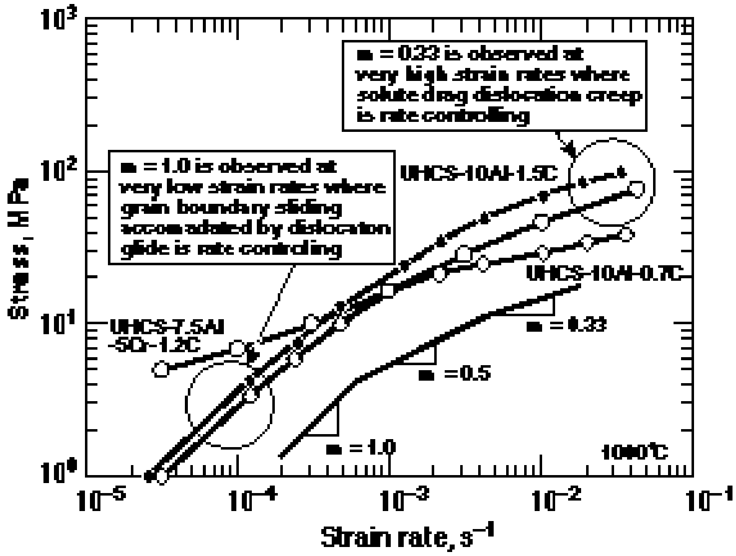


Figure 5. Quasi-superplasticity (m=0.33) and ideal grain-boundary sliding (m=1.0) are observed in UHCS-high Al alloys.

Room Temperature Properties of UHCS Alloys

The UHCS, when processed to develop ultrafine ferrite grains (0.5 to 2 $\mu$m) with fine spheroidized cementite particles, are strong and ductile at room temperature. There is a big drive to create "ultrahigh strength" sheet materials for automotive applications. The primary driver is for weight reduction, which results in enhanced performance and fuel economy. In Fig. 6, the considerable increase in strength of UHCS sheet is illustrated over conventional and advanced automotive steel sheet when such steels are compared at an equivalent tensile ductility.

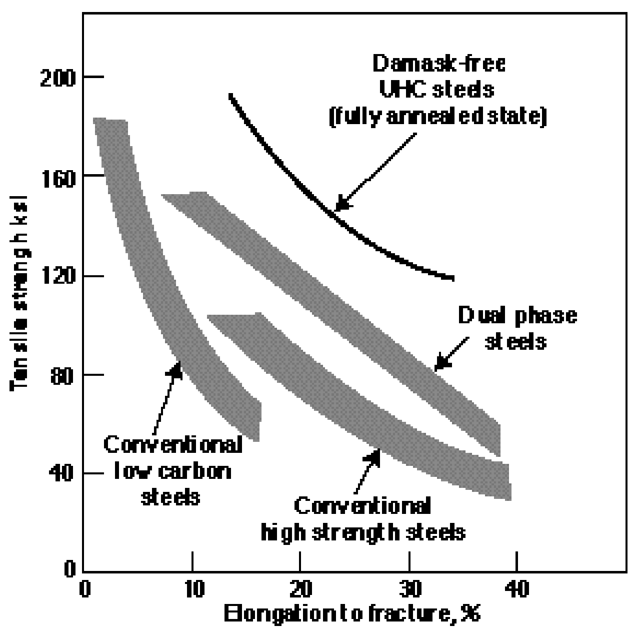


Figure 6. Strength of UHCS sheet compared to conventional and advanced automotive steel sheet.

The current applications that use high carbon steels (0.5 to 1.0%C) are logical candidates for substitution with UHCS. For example, eutectoid composition steels (0.8%C) are typically used for wires for tire reinforcement, cutting tools, and railroad rails. In these applications the UHCS will exhibit higher strengths under comparable microstructural conditions, i.e. in either spheroidized, pearlitic, bainitic, or tempered martensitic form. This is because, with a higher carbon content, the overall microstructural state can be refined.

An unusual result was found for heat-treated UHCS. Toughness was observed in the UHCS in a fine martensitic condition.(14) An example of an austenitizing-and-quenching treatment on the room temperature mechanical properties is shown in Fig. 7. In this figure, compression stress-strain curves for a 1.3%C steel in two conditions are shown with accompanying micrographs. In the first steel, designated as steel A, a fine-grained UHCS, such as the one shown in Fig. 3, was heat treated by quenching into water from a temperature (770°C) just above the $A_1$ temperature. Such a heat treatment, initially producing a fine austenite grain size containing fine cementite particles, results, on quenching, in a microstructure of optically unresolvable martensite containing undissolved cementite particles (Fig. 7). This material, of Rc = 66, exhibits 10% compression ductility and a very high fracture strength of 4500 MPa.

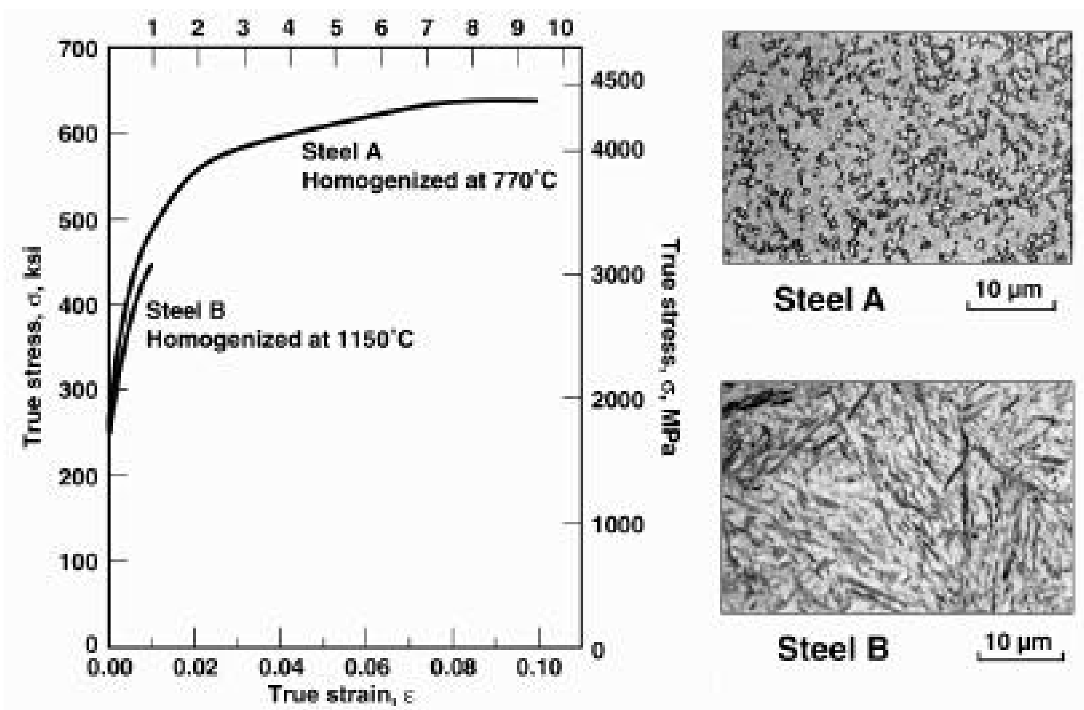


Figure 7. The influence of prior heat treatment on UHCS quenched from 770°C is shown in the above figure.

The second steel, designated as steel B, and also shown in Fig. 7, was quenched from the same low temperature of 770°C, but in this case, it was first austenitized at 1100°C. Such an additional step in the heat treatment results in a coarse martensite and a coarse cementite particle size. By maintaining the same carbon content in the martensite and the same volume fraction of martensite as in steel A, direct comparison can be made of the influence of fineness of microstructure of the quenched structure on the properties of the two steels. The mechanical properties and microstructure of steel B are shown in Fig. 7. This steel, which contains coarse martensite needles, has a similar hardness, Rc = 67, but a low compression fracture strength (3000 MPa) and low ductility (1%). Clearly, ultra-fine-martensitic UHCS would be exceptionally suitable in wear resistant applications such as drill bits, industrial knives, and hand tools.

## Damascus Steels and Ancient UHCS

In 1978, Sherby and Wadsworth were made aware that the typical composition of carbon in UHCS is essentially the same as in Damascus steel swords of ancient times, i.e., about 1.4 to 1.8%C. These weapons were renowned for their fine cutting edge and high toughness; that is, they were highly resistant to cracking. Perhaps even more important, they were famous for the incomparably beautiful surface markings which gave the weapon a mystic and spiritual feel. The method of their manufacture by blacksmiths of ancient times is believed to be a lost and forgotten art. An effort was made to reproduce such markings on UHCS materials, and after success was achieved (15, 16), the published procedure was described as the modern rediscovery of Damascus steel making.

An example of a Damascus steel sword (a Persian scimitar) is shown in Fig. 8. The special surface pattern is a swirly distribution of the proeutectoid carbides (the white areas) achieved by a complex forging procedure. These white regions are different from, but related to, the iron carbide network shown in Fig. 2. The vertical arrays, known as “Mohammed's ladder”, are deliberately created from the different directions of upset forging.

Figure 8. Persian scimitar dating from the 17th century or later in the Metropolitan Museum of Art, New York.

It is believed that the Damascus steel was made in India where it was known as wootz. It was widely traded in the form of castings, or cakes, that were about the size of hockey pucks. The best blades are believed to have been forged in Persia from Indian wootz, which was also used to make shields and armor. These steels were known in the middle ages in Russia where they were called “bulat” steels. In Persia, they were known as “pouhad Janherder”.

The exact procedures used by the ancient blacksmiths in making the surface markings on genuine Damascus steel swords (the term "genuine" is used to distinguish these materials from "welded" structures that in some cases were attempts to duplicate the real materials) have been the source of much speculation. When procedures are described, they are usually given in vague terms, with no precise descriptions of temperature of forging, of the cooling rate prior to and after forging, or of the degree of deformation given at each step. In 1979 (17), a specific procedure was proposed which may have been used by the ancient blacksmiths and has become known as the "Wadsworth-Sherby" method.(18) The procedure utilized is a rolling process involving three key steps.

First, the wootz (in this case, a UHCS containing over 1.5%C) is heated to near its incipient melting point (a white heat ~1200°C) to develop coarse iron grains. Second, the wootz is cooled very slowly, over a period of several hours, to form a thick continuous network of iron carbide at the boundaries of these coarse iron grains. At this point, surface markings are visible to the naked eye consisting of spherical grains with a thick border of iron carbide (Fig. 2). Third, the wootz is heated to a color between blood red and cherry (i.e. about 650 to 750°C), a temperature at which the iron carbide network will not dissolve, and the wootz is then mechanically worked extensively to break the network into individual, coarse, iron-carbide particles that are spherical or elongated . The network is now no longer continuous, but remains visible as a layered structure, and is very appealing to the naked eye.

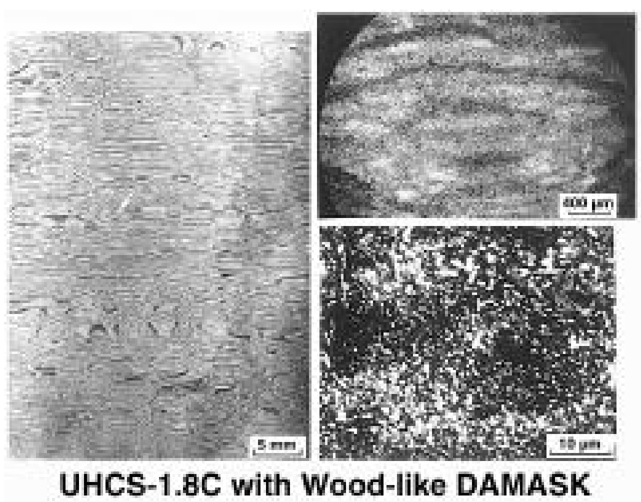


Figure 9. Damask on a UHCS-1.8C material processed by rolling to obtain a wood-like structure. Three magnifications are shown illustrating the severe break-up of the proeutectoid carbides into band-like regions.

Photomicrographs of a UHCS-1.8C material, processed by the "Wadsworth-Sherby" method, are shown in Fig. 9.(19) Photomicrographs are shown at three different magnifications. On the left is a low magnification photomicrograph showing the wood-like pattern. In the top right, at a higher magnification, the dark etching bands are the broken up proeutectoid carbides. The highest magnification photomicrograph, lower right, show the bands of alternating coarse and fine carbides. In order to evaluate the potential for genuine Damascus steels with markings to exhibit superplasticity, tension tests were performed at elevated temperature on the UHCS-

1.8%C material containing a visible damask. The material was found to be superplastic, with an elongation of 450%.

### Modern Laminated Metal Composites (LMCs) Containing UHCS

Early in the development of the monolithic UHCS, it was recognized that toughness was not high. To develop toughness, the concept of lamination was introduced. This led to extensive studies on the impact behavior of laminates containing UHCS, but then also to studies of their tensile behavior at low and high temperature and also their ballistic impact resistance. It was recognized early on in these studies that there were ancient forms of laminated composites that in some cases contained UHCS-type compositions. In this section, the tensile and impact properties of modern LMCs are discussed. Ancient LMCs are described in the next section.

#### Tensile Properties of Laminated Composites

Thick-layer, metal-base, laminated composites are usually prepared by solid state bonding procedures. The bonding step commonly involves mechanical working by pressing, forging, rolling, or extrusion.

It has been shown that the low temperature tensile yield strength of thick layer laminated metal composites based on UHCS and Al-based composites can be readily predicted by the rule of averages.(20-25) This has been shown for metal systems where two components of equal volume fraction have been investigated.

The tensile ductility of laminated composites, on the other hand, cannot be predicted by the rule of averages. The tensile ductility of most of the laminated composites is lower than that predicted from the rule of averages when the difference between ductility of the two components is large. There is also a layer thickness effect on the ductility of laminated composites.(26)

The high temperature tensile behavior of metal laminated composites has been studied for potential superplastic behavior. The studies have shown that a non-superplastic material can be made superplastic by lamination.(27-31) For example, it has been shown that a non-superplastic material (interstitial free iron) could be made superplastic by lamination with a superplastic material (fine grained UHCS). It was shown that the predicted behavior of the composite was readily determined by assuming isostrain deformation of a laminated composite containing two components. A schematic illustration of the laminated composite is given in Fig. 10. The highest elongation achieved in the experimental interstitial free (IF) iron/UHCS composite system was 430% elongation at 650°C in contrast to 100% elongation for IF iron alone.

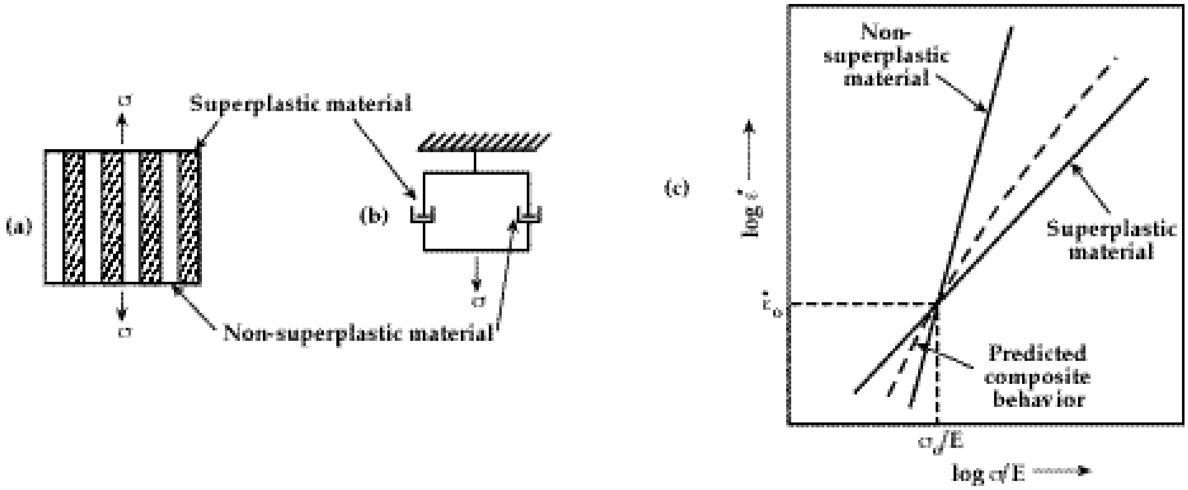


Figure 10. Schematic representations of (a) isostrain testing orientation of laminated composites; (b) mechanical analogy of deformation of two component laminated composite (in isostrain orientation, analogy consists of two dashpots arranged in parallel and subjected to a stress σ); and (c) predicted strain rate-stress behavior of each of the two components and the overall behavior of the laminated composite. Behavior is predicted to follow that of the stronger of the two components.(32)

<u>Impact Behavior</u>

One of the attractions of developing laminated composites is that they can exhibit a very high notch impact resistance. It is this area of property improvement that is perhaps not intuitive in its application to ancient welded laminated products.

In the area of notch impact resistance, high impact strengths have been obtained in laminated composites based on UHCS. A dramatic example is shown in Fig. 11 for a UHCS/mild steel laminate.(33) It is worth noting that each of these monolithic samples was thermo-mechanically processed in an identical manner to the corresponding individual steel layers in the laminated composite. The Charpy V-notch impact properties for these materials (i.e. the 12-layer laminated composite of UHCS/mild steel, the monolithic UHCS, and the monolithic mild steel) are very different. The laminated composite in the crack arrester orientation showed greatly improved impact resistance characteristics compared with either of the monolithic steels. For example, the upper shelf energy of the UHCS/mild steel laminated composite is ~325J compared with 190J for the monolithic mild steel and 75J for the monolithic UHCS. In addition, the 20J ductile-to-brittle transition temperature (DBTT) is –150°C for the laminated composite compared with –100°C for the monolithic mild steel and 0°C for the UHCS.

The dramatic improvement in the impact properties of the laminated composite is a result of notch blunting by extensive delaminations that occur on either side of the initial crack direction in all samples. The samples, however, remained intact and delamination was confined to the center regions adjacent to the initial crack direction. The ability to delaminate is a key factor in controlling the impact characteristics of the laminated composite.

The above hypothesis was tested by heat treating samples of the UHCS/mild steel laminated composite to above the $A_1$ temperature to improve the bond strength.

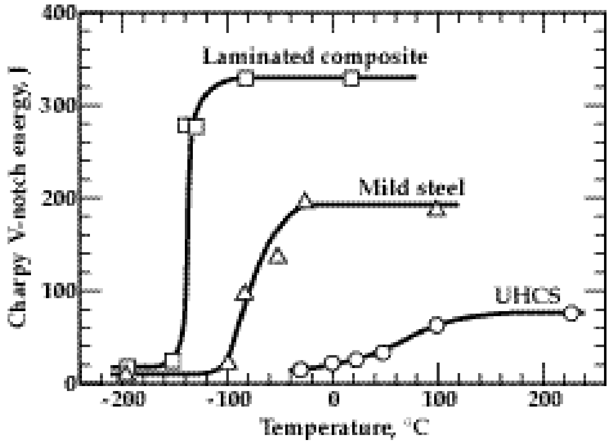


Figure 11. Charpy V-notch impact test results for 12-layer laminated composite of UHCS/mild steel in crack arrester orientation and for mild steel and UHCS monolithic steel.(33)

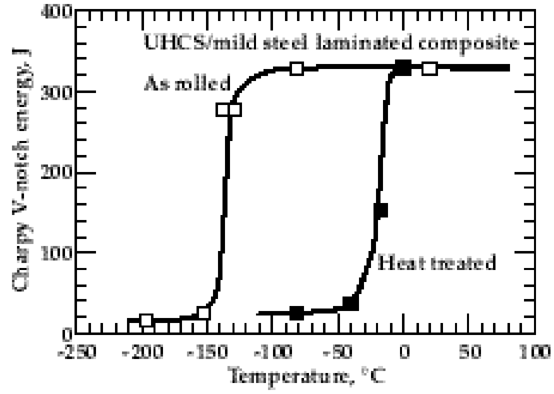


Figure 12. Charpy V-notch impact test in crack arrester orientation for 12-layer laminated UHCS/mild steel composites, both in as-rolled (weak interfaces) and heat-treated (strong interfaces) conditions. Degradation of impact properties occurs as result of heat treatment.(33)

The results are shown in Fig. 12. Also shown are the results on the as-rolled samples (weak interfaces) taken from Fig. 11. The impact properties of the laminated composite are significantly degraded by heat treatment. Macrographs of these samples are shown in Fig. 13. It is clear that delamination is significantly reduced following heat treatment. It was concluded that the loss in impact strength following heat treatment is a result of improving the interface strength.

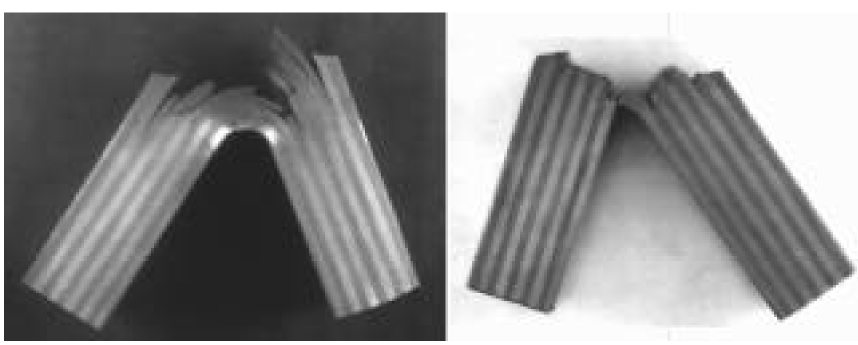

Figure 13. Macrographs comparing fracture behavior at –79°C for 12-layer laminated UHCS/mild steel composite. Extensive delamination occurs in (left) as-rolled (weak interfaces) condition, but is absent in (right) heat-treated (strong interfaces) condition.(33)

It is therefore implied in Figs. 11 and 12 that the excellent Charpy V-notch properties of the as-rolled laminated composite in the crack arrester orientation are a result of the effects arising from delamination (e.g. by crack blunting or increased energy absorption during delamination). If this is so, then the composition of the interleaf material in laminated composites containing UHCS should not have a great influence on their impact properties. To test this proposal, the mild steel layers in the UHCS/mild steel laminated composite were replaced with UHCS layers. The impact properties of such a UHCS laminate were indeed similar to the UHCS/mild steel laminated composite.

In recent years, the precise role of the interleaf materials — for example, Hadfield manganese steel (HMS) (34), nickel-silicon steels (35), and brass (36) — on the impact properties of UHCS has been studied in more detail. The UHCS/brass combination provides the best impact properties at low temperature. This is because brass does not exhibit a DBTT and thereby contributes to the blunting of propagating notches.

The response of metallic laminates to ballistic impact has also been studied by several investigators (37-40) and, in general, the results have shown that laminate plates can be designed to increase the amount of energy absorbed during impact and thus improve the material resistance to penetration, perforation, and spall relative to non-laminated targets.

Toughening mechanisms in LMCs can arise from many different sources. Recent work has shown that toughening in materials can result from two different types of mechanisms — intrinsic and extrinsic.(41, 42) Intrinsic toughening results from the inherent resistance of the microstructure to crack growth and thus is influenced by such microstructural characteristics as grain size, particle spacing, particle size, etc. Extrinsic toughening, on the other hand, results from mechanisms that reduce the local stress intensity at the crack tip and thus the local "driving force" for crack growth. The distinct layers present in LMCs toughen these materials by various extrinsic mechanisms. Numerous extrinsic and intrinsic toughening mechanisms have been identified in composites and monolithic materials (41, 42), and these can provide additional sources of toughening in LMCs. (Included are crack deflection, crack blunting, crack bridging, stress redistribution, crack front convolution, and local plane stress deformation.)

The work thus far on toughening in LMC systems clearly indicates that different mechanisms are dominant depending on the orientation of the crack relative to the layer architecture. In the crack arrester orientation, it appears that crack blunting and deflection are the dominant mechanisms, and can produce appreciable increases in toughness.

In the crack divider orientation, increases in fracture toughness relative to unlaminated systems have tended to be more modest. The dominant mechanisms in this case are crack front convolution and local plane stress deformation. Further improvements in the toughness in the crack divider orientation are desirable as this is often the key orientation for many structural applications.

It is difficult to generalize about the benefits of lamination with respect to fracture resistance in ancient artifacts. Clearly, some of the above mechanisms could well apply. However, it is probably necessary to evaluate each ancient material for such fracture resistance improvements. The Japanese sword for example is a laminate at several levels.

Examples of modern laminates containing UHCS, including commercial materials and Former Soviet Union materials are given in Table I. It is worth noting that the practical application of LMCs is far more developed in the Former Soviet Union than in the western world. Applications include the use of laminated materials for fracture critical applications involving large pipes (43), large pressure vessels (44), and gun tubes (44). Materials include steels, white cast irons, and Al-based alloys. Such modern laminated metal composites can be made by many techniques, such as bonding, deposition, and spray forming.

Table I. Some Examples of Modern Laminated Composites

| Material | Approximate Era | Composition (where known) | |
|---|---|---|---|
| | | Layer A | Layer B |
| UHCS Mild Steel | 1979 - Present | 1%C | AISI 1020, 0.2%C |
| UHCS Interstitial Free Iron | 1984 | UHCS | ~0%C |
| UHCS HMS | 1990 | UHCS | Hadfield manganese steel |
| UHCS Ni/Si | 1992 | UHCS | Ni – Si |
| UHCS Brass | 1992 | UHCS | Al – bronze, brass 70%Cu – 30%Zi |
| UHCS 304 SS | 1997 | UHCS | 304 stainless steel |
| UHCS Fe – 3 Si | | UHCS | Fe – 3%Si |
| Former Soviet Union Oil Pipes | Present | oil pipe steel | same composition |
| Former Soviet Union Explosive Forming | Present | tool steel/tool steel | Cu/Al |
| Moscow Steel and Alloy Institute Concentric Tubes | Present | 2.1 – 2.6%C | 0.6%C |
| Modern Japanese Sword | Present | see ancient Japanese Sword | |
| Norwegian 3-layer Blades and Japanese Chisels | Present | A – B – A laminate type<br>A – low carbon or stainless<br>B – high carbon tool steel | |
| Modern Damascus Steel Pattern Welded Knives | 1970 - Present | See Table II | |

Table II. Types of Modern Welded Damascus Steel (45)

| | | | |
|---|---|---|---|
| 64-Layer | Composite Twist | O1/L6 | Ferguson |
| 320-Layer | Hand-Smelted Sagami School | 203E/1095 | Meier |
| 500-Layer | Ladder Pattern | Saw Blade | Norris |
| 1000-Layer | Mosaic (100% Ni and wrought iron) | Saw Steel, Wire Rope, and Chain | Rados, Jerry |
| Blue-Stacked | Nickel | Scrap | Raymond, Donald |
| Brass/Steel | Nickel Steel/W1 | Stainless | Schneider |
| Cable | O1/1018 | Tool Steel | Thomas |
| Chain (Motorcycle, Saw) | O1/1095 | Turkish | Thomas, Devin |
| Commercial | | Welded Pattern | Warren, Dellana |
| | | Wire | Zowada, Tim |

## Ancient Laminated Metal Composites

A summary is given in Table III of the evolution of ancient laminated composites. As shown in the table, laminated metal composites have been cited in antiquity; for example, a steel laminate that may date as far back as ~2600 BC, was found in the Great Pyramid in Gizeh in 1837. A laminated shield containing bronze, tin, and gold layers is described in detail by Homer. Well-known examples of steel laminates, such as an Adze blade, dating to 400 BC can be found in the literature. The Japanese sword is a laminated composite at several different levels and Merovingian blades were composed of laminated steels. Other examples are also available, including composites from China, Thailand, Indonesia, Germany, Britain, Belgium, France, and Persia.

Table III. Some Examples of Ancient Laminated Composites

| | | Composition (where known) | |
|---|---|---|---|
| Material | Approximate Era | Layer A | Layer B |
| Gizeh Pyramid Laminated Steel Plate | ~2600 BC | low carbon steel ~0.2%C | wrought iron |
| Achilles' Shield | 700-800 BC | 5-layer composite of bronze/tin/gold/tin/bronze | |
| Adze Blade (Turkey) | 400 BC | medium carbon steel ~ 0.4%C | low carbon backing plate ~0.1%C |
| Chinese Blade "Hundred Refinings" | 100 AD onward | negligible | low carbon |
| Merovingian Blade | $2^{nd}$ - $12^{th}$ century AD | carbon steel | "pure" iron |
| Japanese Sword | 400-500 AD to present | | |
| Overall Blade | | outer sheath: 0.6 - 1.0%C | inner core: 0 - 0.2%C |
| Outer Sheath — Initial to Final Condition | | 1.6%C reduced during 12 - 20 foldings (see text) to 0.6 - 1.0%C | interlayer regions during final foldings may be low in C due to decarburization |
| Thailand Tools | 400-500 AD | negligible | 0,13, 1.8(?)%C |
| Indonesian Kris | $14^{th}$ century AD onward | tool steel ~1%C | low carbon; meteoric iron (Fe – 5 - 7%Ni) |
| Halberd | 14th century AD onward | high carbon | low carbon (complex assembly) |
| Chinese Pattern Welded Blade | $17^{th}$ century AD | unknown | unknown |
| Shear Steel and Double Shear Steel | $19^{th}$ century AD | high carbon | mild carbon |
| European Gun Barrels | $19^{th}$ century AD | steel ~0.4%C ? | low carbon steel or pure iron |
| Persian Dagger | $19^{th}$ century AD | ~0.8%C | ~0.1%C |

The motivations for laminating metals are varied. For example, in carburizing the earliest forms of wrought iron, only thin layers could be carburized and so lamination was a way to create bulk material. (This could be the motivation for the most ancient laminates.) Another reason is that the hard material, steel, was rare and it was expedient to sandwich it between more common materials. (This motive is found in medieval knives.) From a mechanical viewpoint, optimizing the combination of strength, toughness, and sharpness is the basis for lamination. (Examples include the Japanese sword, the Halberd, and modern laminates.) Finally, there is a strong motivation based on decorative appeal. (Many modern knives are made in laminated form for this reason, but it could have been a motive in ancient knives also.) Further details on these ancient laminates are given in recent papers.(46) Some examples of these ancient laminates are given in Figs. 14-18.

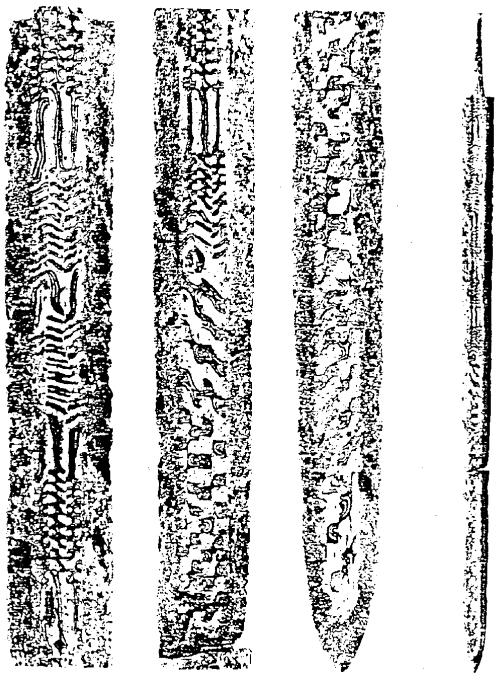

Figure 14. Merovingian pattern-welded blade discovered in a Viking grave in the South of Finland. It was most likely made on the Rhine in the period 650-700 AD.(43)

Figure 15. "O-Kanehira." *Tachi* by Kanehira. 89.2cm. Mid-Heian period, approximately 1000AD. Tokyo National Museum. Signed *Bizen no kuni Kanehira* ("Kanehira of Bizen providence").(47)

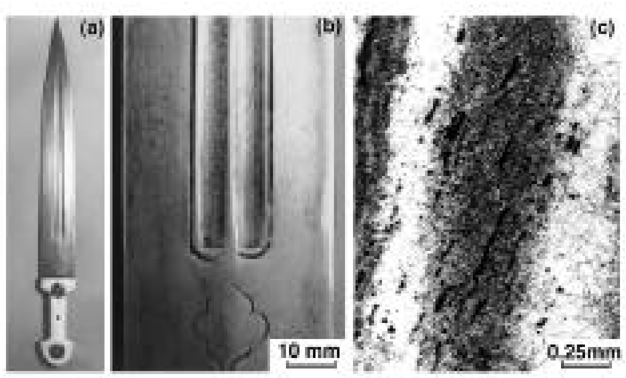


Figure 16. Welded Damascus steel dagger. (a) dagger; (b) unique surface markings, low magnification; (c) micrograph showing distinct layers of high carbon spheroidized steel (dark) and low carbon steel (light).(32)

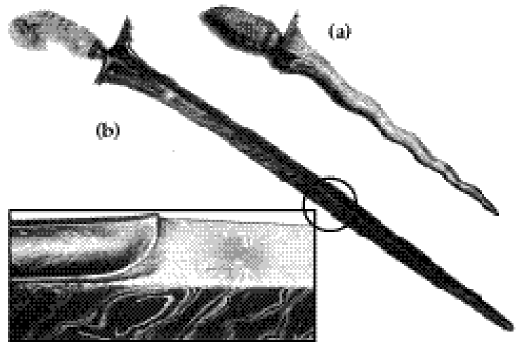

Figure 17. Krisses. (a) Typical Indonesian kris. (b) Indonesian executioner's kris is a composite of meteoric nickel iron and plain carbon steel.

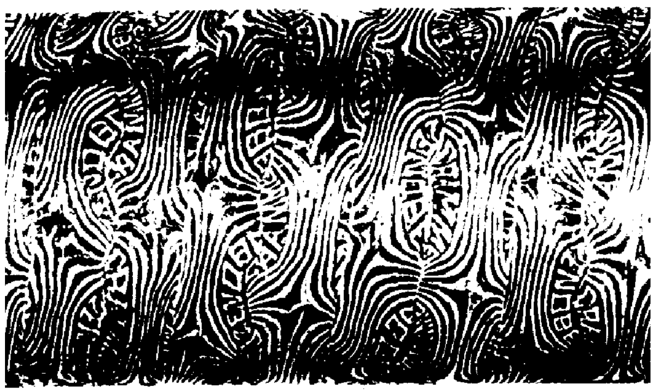

Figure 18. Welded Damascus gun barrel with the words zenobe gramme worked into the pattern. This advanced stage of development was reached in the 19th century.(43)

**The History of Steels**

The work on Damascus steels has stimulated our interest in the history of other steels and steel laminates. No one really knows when steels were first deliberately developed. The wisdom found in contemporary books on the subject suggests about 1500 BC; but, this date is quite uncertain. In part this is because iron and steel rust with time, and unlike copper artifacts, are not usually found in significant quantities before 1500 BC. In some cases, dates of origin of iron and steel can go far further back in time, up to as far as 4000 to 5000 BC as described in the following.

El Gayer and Jones (48) have recently summarized the possible early sources of iron. These include (a) meteoric iron derived from extra-terrestrial sources; (b) native iron produced by natural, terrestrial processes; (c) by-product iron formed, in small quantities, when iron-rich copper ores are used to produce copper metal; in sources (a), (b), and (c), dates of use can go back to 4000-5000 BC; (d) ancient wrought iron deliberately produced by the comparatively low temperature, solid-state reduction of iron oxide with charcoal and, much later, with coke; and (e) cast iron produced by using much higher smelting temperatures than those used for producing wrought iron. It is commonly accepted that the first known activity in iron and iron-carbon alloys occurred in the Middle East and in the nearby countries of India, Ceylon, and

Egypt. For example, in the Ankara Technological Museum, there is on exhibit an iron dagger which is dated as 2500 BC, but the authenticity of this date is quite uncertain. In another example, one of the more perfectly preserved sets of iron objects (a dagger, an iron headrest, and an amuletic bracelet) was found in the tomb of Tutankhamen who ruled Egypt from 1361-1352 BC. In a third example (49), in the *Rig Veda* (the sacred book of India compiled from 3500-1800 BC), it is described how Queen Vishpla lost a leg during battle and that, following healing, she was fitted with an iron leg in order to return to battle. In addition to the above examples, there is a specific interest in a laminated iron plate found at the Great Pyramid of Gizeh; the Pyramid was built about 2600 BC.

In 1837, an iron plate (26 cm x 86 cm x a maximum thickness of 0.4 cm) was discovered by an excavation team near an air passage (Southern side) in the Great Pyramid at Gizeh, Egypt. The location of the plate was within an undisturbed section high up on the Pyramid. The plate was removed to the British Museum and was not examined for its structure until El Gayer and Jones used modern metallographic techniques and published their findings in 1989.(48) A comment by Craddock and Lang (50) was included in the same issue of the Journal.

The significance of the plate is twofold. First, if it can be shown to be contemporaneous with the building of the Pyramid, then it is one of the oldest known plates of iron metal ever discovered and dates from the 4th Dynasty, circa 2600 BC. Second, the metallographic study of El Gayer and Jones revealed that the plate consisted of:

> "...numerous laminates of wrought iron and that these laminates have been inexpertly welded together by hammering. The various layers differ from each other in their grain sizes, carbon contents, the nature of their non-metallic inclusions, and in their thicknesses."

It was further deduced from elongated non-metallic inclusions that the welding process had been carried out at modest temperatures (~800˚C) allowing re-crystallization of the iron matrix grains. The absence of metallic copper globules and only small traces of elemental copper suggested that the plate had not been produced as a by-product of copper smelting operations of iron-rich copper ores. Also, a chemical analysis reported in 1926 revealed only trace levels of nickel, thereby confirming the plate to be of terrestrial (but not natural) origin rather than to be meteoric.(48) (It is noted that the above view on lamination is not universally agreed upon. An alternate view is that the heterogeneous nature of the plate is a direct result of a heterogeneous starting piece.(51))

Summarizing, El Gayer and Jones concluded that the iron pieces comprising the laminate were:

> "...intentionally produced during small-scale (and, possibly, very primitive) operations primarily designed for the production of iron metal (rather than copper metal). Furthermore, the presence of abundant inclusions of unreduced (or incompletely reduced) fragments of iron oxides in the metal laminations shows that the 'smelting' operations had been inexpertly carried out at low

temperatures (probably between 1000 and 1100˚C) and that the iron had been produced by the 'direct reduction' method – in which no molten iron is normally produced."

And, most importantly, they also concluded:

"Furthermore, the metallurgical evidence supports the archaeological evidence which suggests that the plate was incorporated within the Pyramid at the time that structure was being built."

Although accounts by the excavation teams emphasize the fact that the plate was found within the Pyramid, and is therefore contemporaneous with the Pyramid, this view has not been generally accepted by archeologists. Resolving the issue of the date of manufacture of the iron plate is, therefore, of great interest.

The possibility does exist to directly measure the age of ancient steel artifacts by $C^{14}$ dating. Until relatively recently, the technique required large amounts of carbon, rendering the process impractical for rare and scarce samples. However, with the advent of accelerator mass spectrometry and refinements in the techniques, dating can now be accomplished on very small amounts of material. Some work on direct dating on small samples has been demonstrated in the last few years. The author and a colleague (52) have recently been establishing this capability at the Lawrence Livermore National Laboratory. When initial studies are complete, and the accuracy demonstrated for artifacts of known age, it may be appropriate to use the technique to resolve issues regarding the age of materials older than 1500 BC to resolve controversies regarding the date at which significant quantities of iron-based materials were made. The basis of the technique relies on the incorporation of contemporaneous carbon into the material and of necessity is therefore limited to steels rather than pure iron. Examples such as the laminated plate at Gizeh may be addressed with this method.

## Conclusions

UHCS containing between 1 and 2%C were developed by Oleg D. Sherby and his colleagues at Stanford University starting in 1975. The UHCS can be processed to have unique engineering properties. These are of interest both in terms of formability (i.e. superplasticity) at high temperature and also strength and ductility at room temperature. The steels have similar compositions to ancient Damascus steels. It has been demonstrated that modern UHCS can be developed to have surface patterns similar to ancient steels and that such patterned steels exhibit superplasticity; this raises the possibility that ancient Damascus steels were superplastic.

Modern laminated composites containing UHCS were also developed and exhibit excellent impact toughness. An improved understanding of room-temperature strength and toughness of laminated composites has been developed. Under key conditions of strain rate and temperature, these laminates also can exhibit superplastic properties. Laminated composites were also made in ancient times and in many cultures, and these are described.

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**References**

1. Wadsworth, J., and O.D. Sherby in Thermomechanical Processing and Mechanical Properties of Hypereutectoid Steels and Cast Irons, eds. D.R. Lesuer, C.K. Syn, and O.D. Sherby (The Minerals, Metals & Materials Society, 1997).
2. Syn, C.K., D.R. Lesuer, and O.D. Sherby, Metallurgical Transactions 24A (1993) 1481-1493.
3. Sherby, O.D., T. Oyama, D.W. Kum, B. Walser, and J. Wadsworth, Journal of Metals 37 (6) (1985) 50-56.
4. Lesuer, D.R., C.K. Syn, A. Goldberg, J. Wadsworth, and O.D. Sherby, Journal of Metals 45 (8) (1993) 40-46.
5. Kayali, E.S., H. Sunada, T. Oyama, J. Wadsworth, and O.D. Sherby, Journal of Materials Science 14 (1979) 2688-2692.
6. Oyama, T., J. Wadsworth, M. Korchynsky, and O.D. Sherby in Strength of Metals and Alloys, eds. P. Haasen, V. Gerold, and G. Kostorz (Aachen: Pergamon Press, Oxford, 1979) Vol. 1, 381-386.
7. Wadsworth, J., and O.D. Sherby, Journal of Mechanical Working Technology 2 (1978) 53-66.
8. Wadsworth, J., and O.D. Sherby, Journal of Materials Science 13 (1978) 2645-2649.
9. Wadsworth, J., J.H. Lin, and O.D. Sherby, Metals Technol. 8 (1981) 190-193.
10. Kayali, E.S., "Superplasticity of Eutectoid Seel and Iron-Carbon Alloys" (PhD Dissertation. Department of Materials Science and Engineering, Stanford University, Stanford, CA, 1976).
11. Walser, B., E.S. Kayali, and O.D. Sherby in Proceedings of the 4th International Conference on Strength of Metals and Alloys. Nancy, France, 1976, 1, 456-460.
12. Fukuyo, H., H.C. Tsai, T. Oyama, and O.D. Sherby, ISIJ International 31 (1991) 76-85.
13. Sherby, O.D., T.G. Nieh, and J. Wadsworth in Materials Science Forum, ed. T.G. Langdon (Switzerland: Trans Tech. Publications, 1994) Vol. 170-172, 13.
14. Sunada, H., J. Wadsworth, J.H. Lin, and O.D. Sherby, Materials Science and Engineering 38 (1979) 35-40.
15. Wadsworth, J., and O.D. Sherby, Progress in Materials Science 25 (1980) 35-68.
16. Sherby, O.D., and J. Wadsworth, Scientific American 252 (2) (1985) 112-120.
17. Wadsworth, J., and O.D. Sherby, Annual Bulletin of the Metals Museum 4 (1979) 7-23.
18. Wadsworth, J., and O.D. Sherby, Materials Characterization 28 (2) (1992) 165-172.

19. Sherby, O.D., and J. Wadsworth, SAMPE Journal 31 (4) (1995) 10-17.

20. Syn, C.K., S. Stoner, D.R. Lesuer, and O.D. Sherby in High Performance Metal and Ceramic Composites, ed. K. Upadhya (Warrendale, Pennsylvania: TMS, 1994), 125-136.

21. Chawla, K.K., and C.E. Collares in International Conference on Composite Materials. Warrendale, Pennsylvania, 1978. TMS, 1237-1245.

22. Lee, S., J. Wadsworth, and O.D. Sherby, Journal of Composite Materials 25 (1991) 842-853.

23. Sherby, O.D., S. Lee, R. Koch, T. Sumi, and J. Wolfenstine, Materials and Manufacturing Processes 5 (1990) 363-376.

24. Syn, C.K., D.R. Lesuer, and O.D. Sherby in Advanced Synthesis of Engineered Structural Materials, ed. J.J. Moore, et al. (Materials Park, Ohio: ASM International, 1992), 149-156.

25. Syn, C.K., D.R. Lesuer, and O.D. Sherby, Materials Science and Engineering A206 (1996) 201-207.

26. Syn, C.K., D.R. Lesuer, J. Wolfenstine, and O.D. Sherby, Metallurgical Transactions 24A (1993) 1647-1653.

27. Snyder, B.C., J. Wadsworth, and O.D. Sherby, Acta Metallurgica 32 (1984) 919-932.

28. Daehn, G.S., "Superplasticity Instability in Metal-based Composites" (PhD. Engineering, Stanford University, Stanford, California, 1988) 3781 1988D.

29. Daehn, G.S., D.W. Kum, and O.D. Sherby, Metallurgical Transactions 17A (1986) 2295-2298.

30. Tsai, H.C., J. Wolfenstine, and O.D. Sherby, Composites 22 (1991) 373-379.

31. Tsai, H.C., K. Higashi, and O.D. Sherby in International Conference on Advanced Composite Materials. Warrendale, Pennsylvania, 1993. TMS, 1287-1293.

32. Lesuer, D.R., C.K. Syn, O.D. Sherby, J. Wadsworth, J.J. Lewandowski, and W.H. Hunt, Jr., International Materials Reviews 41 (5) (1996) 169-197.

33. Kum, D.W., T. Oyama, J. Wadsworth, and O.D. Sherby, Journal of Mechanics and Physics of Solids 31 (2) (1983) 173-186.

34. Lee, S., J. Wadsworth, and O.D. Sherby, Res. Mechanica 31 (1990) 233-248.

35. Lee, S., J. Wadsworth, and O.D. Sherby, Journal of Engineering Materials Technology 114 (1992) 278-281.

36. Lee, S., T. Oyama, J. Wadsworth, and O.D. Sherby, Materials Science and Engineering A154 (1992) 133-137.

37. Chitkara, N.R., and M.K. Wong in International Symposium on Intense Dynamic Loading and Its Effects. Beijing, 1986. Science Press-Beijing, 352-363.

38. Woodward, R.L., S.R. Tracey, and I.G. Crouch, Journal of Physics, IV 1 (1991) 277-282.

39. Woodward, R.L., and I.G. Crouch, "Analysis of the Perforation of Monolithic and Simple Laminate Aluminium Targets as a Test of Analytical Deformation Models" (Report MRL-R-1111, Australian Defence Science and Technology Organisation, Melbourne, Victoria, 1988).

40. Riddle, R.A., D.R. Lesuer, C.K. Syn, R. Gogolewski, and B. Cunningham, Finite Elements in Analysis and Design 23 (1996) 173-192.

41. Ritchie, R.O., and W. Yu in Small Fatigue Cracks, eds. R.O. Ritchie and J. Langford (Warrendale, Pennsylvania: TMS, 1986), 167-189.

42. Ritchie, R.O., Materials Science and Engineering A103 (1988) 15-28.

43. Sherby, O.D., and J. Wadsworth, SAMPE Journal 31 (1995) 32-39.

44. Hertzberg, R.W., Deformation and Fracture Mechanics of Engineering Materials (New York: Wiley, 1983) Vol. 25, 328-330.

45. Warner, K., ed., 18th Annual Edition, Knives '98 (Wisconsin: DBI Books Inc., 1997).

46. Wadsworth, J., and D.R. Lesuer, "Ancient and Modern Laminated Composites — From the Great Pyramid of Gizeh to Y2K" (Metallography, History, and the Fine Arts Symposium, International Metallographic Society (ISM) 1999 Conference, International Metallographic Society, Cincinnati, Ohio, October 31, 1999).

47. Sato, K., The Japanese Sword. Translated and adapted by Joe Earle. *Japanese Arts Library*, ed. J. Rosenfield (Tokyo and New York: Kodansha International and Shibunda, 1983).

48. El Gayar, E.S., and M.P. Jones, Journal of the Historical Metallurgy Society 23 (2) (1989) 75-83.

49. Duraiswami, P.K., and S.M. Tuli, Clinical Orthopedics and Related Research 75 (1971) 269-280.

50. Craddock, P., and J. Lang, Journal of the Historical Metallurgy Society 23 (2) (1989) 123.

51. Goodway, M., personal communication, Suitland, Maryland: Smithsonian Center for Materials Research and Education, July, 1999.

52. Wadsworth, J., and A.C. Cook, work in progress, 1999.